THE FATE OF SOME TRACE ELEMENTS DURING COAL PRETREATMENT AND COMBUSTION

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INTRODUCTION

Why should we interest ourselves in trace metals in coals? Fact #1: There are a number of elements known to be of high toxicity in coal, most of them present in trace amounts. Fact #2: Over 300 million tons of coal was burned in the United States last year for the generation of electric power. When we put the two facts together, we realize that we are talking of a total of tons; hundreds of tons or even thousands of tons of toxic elements present in the coal we burn for power generation. How much of these toxic elements are present in the coal we burn for power generation? How much of these toxic trace elements enters the environment via the smoke stacks of powerplants?

Today I would like to discuss two trace-element studies being carried out at the Pittsburgh Energy Research Center of the Federal Bureau of Mines. The first program, which is funded by the Bureau, is involved in elucidating the fate of the various toxic trace elements present in coal when the coal is burned in powerplants. The second program is funded by the Environmental Protection Agency and is concerned with investigating the distribution of the trace elements in coal using specific gravity separations to divide the coal into discreet fractions.

The two programs taken together can give us a picture of what happens to the trace elements in coal from the coal bed to the powerplant stack. Both investigations are still in progress, so today's talk is really an interim report. I would like to cover the problems we have encountered, the results we have obtained, and any conclusions we have drawn from the results.

The elements that we are currently studying in the EPA program are mercury, copper, chromium, manganese, nickel, and fluorine. In the Bureau program, studies so far have been limited to mercury, cadmium, and lead.

Let us elucidate some of the general problems one encounters in analyzing coal for its trace element content. Except for the special case of mercury, there is no standard coal presently available for use in trace-element analysis. Because the precision and accuracy of the analytical procedures used are in many cases affected by the matrix one is dealing with, the lack of a standard coal is a serious problem.

Contamination is another problem one encounters in trace analysis. Mercury is ubiquitous in many laboratories as is fluoride. Lead is present in dust particularly if your laboratory is close to automobile traffic.

EXPERIMENTAL APPROACH

A. Coal pretreatment study. Selected coals were crushed and separated in organic fluids of known specific gravity. The head (i.e., starting) coal and each specific gravity fraction were analyzed for the trace element or elements being studied and their distribution noted.

B. Combustion study. Coal was combusted in a 100-g/hr combustor, and the ash and flue gases were collected and analyzed for the trace element being studied. After completion of the initial study with the 100-g/hr combustor, coal and ash were obtained from a 500-lb/hr furnace and finally from commercial powerplants. The samples were analyzed

for the trace elements being studied, and the maximum amount of the element that could
be released was calculated.

ANALYTICAL METHODS

A. Mercury. Mercury is determined in coal by means of a double gold amalgamation-
flameless atomic absorption procedure. Because mercury is volatile and can thus be
quantitatively separated from the coal matrix, calibration can be accomplished with
mercury-saturated air. Mercury is the only trace element for which there is presently
an NBS certified standard coal. We normally use mercury-saturated air for calibration
purposes on a day-to-day basis and periodically analyze the NBS standard coal in order
to check our procedure. Table 1 shows some of the results we have obtained with the
NBS standard coal.

Table 1
Analysis of NBS SRM No. 1630
NBS certified mercury value = 0.126 $\pm$0.006 ppm Hg

Dates	Number of replicates	Bureau value
2/24/72	5	0.12 $\pm$0.02
4/19/72	5	.12 $\pm$.01
7/5/72	6	.14 $\pm$.02
9/24/72 through 12/13/72	39	.13 $\pm$.03
2/1/73 through 3/2/73	37	.13 $\pm$.02

As you can see, agreement is very good.

B. Fluorine. Fluorine in coal is determined by combusting the coal in the presence of
calcium oxide, fusing the residue with Na_2CO_3, leaching the melt with phosphoric acid,
distilling the solution with H_2SO_4, concentrating the fluoride by passing the solution
through an anion exchange resin (Amberlite IRA 410), and determining the fluoride
content of the solution with a fluoride specific ion electrode. An NBS opal glass
standard is frequently carried through the entire procedure to check fluorine recovery.

C. Copper, chromium, manganese, and nickel. The analytical method for the determina-
tion of copper, chromium, manganese, and nickel involves digestion of the coal with
HNO_3 and $HClO_4$, fusion of the residue with lithium metaborate, and determination of the
combined digestion and leach solutions by atomic absorption spectrophotometry. Since
there is no standard material to analyze for the construction of calibration curves,
the method of standard additions is employed for the assay. While the method of
standard additions does increase the time required for the analysis, it eliminates the
effect of the matrix.

D. Cadmium and lead. Cadmium and lead are determined in coal by ashing the coal at
500° C, treating with HF and HCl, fusing the residue with K_2CO_3, evaporating to near
dryness, dissolving in HCl, adding Kl and ascorbic acid, extracting into MIBK, and
analyzing for Pb and Cd by means of atomic absorption. Blanks are carried through the
entire procedure, and the method of standard additions is used for calibration.

RESULTS

A. <u>Mercury.</u> An Indiana V strip coal from Indiana and a Lower Kittanning strip coal
from Pennsylvania were separated into four specific-gravity fractions and analyzed for
their trace mercury content. The results are shown in tables 2 and 3. It is clear
that mercury tends to concentrate in the mineral matter and probably exists in coal as
an inorganic compound.

Table 2
Coal - Lower Kittanning Bed, Pennsylvania, strip coal
Mercury content of coal = 0.26 ppm

Specific gravity	Weight-percent	Mercury content, ppm	Percent of total mercury in fraction
Float - 1.30	20.0	0.16	12
1.30 - 1.40	28.1	.23	25
1.40 - 1.60	24.8	.19	18
Sink - 1.60	27.1	.43	45

Table 3
Coal - Indiana V Bed, Indiana, strip coal
Mercury content of coal = 0.13 ppm

Specific gravity	Weight-percent	Mercury content, ppm	Percent of total mercury in fraction
Float - 1.30	42.6	0.08 ± 0.03	29 ± 11
1.30 - 1.40	36.3	$.07 \pm .03$	22 ± 9
1.40 - 1.60	13.7	$.15 \pm .03$	15 ± 3
Sink - 1.60	7.4	$.59 \pm .05$	34 ± 3

Table 4
100-g/hr combustor: Summary of results

Coal[4]	Run	Coal feed rate, g/hr	Combustion efficiency, percent	Fly ash production rate, g/hr	Coal, $\mu g/g$	Fly ash, $\mu g/g$	Flue gas $\mu g/m^3$	Total mercury in fly ash, percent	Total mercury accounted for, percent
DRB-E	1	98.1	97.6	9.1		0.97 ± 0.05	2.2	60	77
DRB-E	2	105.1	97.0	10.4	[1] 0.15 ± 0.02	$.83 \pm .13$	6.5	55	101
DRB-E	3	108.1	96.4	11.3		$.95 \pm .09$	1.7	66	78
P-3	1	98.9	97.5	23.8		$.31 \pm .04$	7.4	31	62
P-3	2	135.7	96.3	34.3	[2] $.24 \pm .05$	$.35 \pm .06$	([3])	37	([3])
P-3	3	117.2	98.3	27.1		$.37 \pm .04$	14.4	36	94

(Mercury content column header: $(\pm 1$ standard deviation))

[1] Average value of 12 replicates for DRB-E.
[2] Average value of 21 replicates for P-3.
[3] No flue gas sampling on this run.
[4] DRB-E is a washed deep-mined Pittsburgh seam coal originating in Washington County,
Pa. P-3 is a mixture of Tebo seam and Weir seam coals from Henry County, Mo.

Table 4 shows the results obtained with the 100-g/hr combustor. Table 5 shows the
results obtained with the 500-1b/hr combustor. Table 6 shows the analyses of the coals
used in the combustion experiments with the 100-g/hr and 500-1b/hr combustors. Table 7
shows the results obtained with power plant samples. The terms MR, DRB-E, and P-3 are
those employed by the engineers running the combustors to identify series of runs under
slightly different conditions but using the same coal.

Table 5
500-1b/hr combustor: Summary of results

Mercury in coal (MR)[1/] ..... μg Hg/g coal ..... 0.18 ± 0.04
Number of replicates 23
Mercury in fly ash .... μg Hg/g ash ...... 0.22 ± 0.04
Number of replicates 17
Percent of total mercury found in fly ash ..... 12 ± 3

[1/] MR is a Pittsburgh seam coal from Pennsylvania.

Table 6
Analysis of coals combusted (mf basis)

	DRB-E	P-3	MR
Proximate analysis, weight-percent:			
Volatile matter	35.8	37.8	37.7
Fixed carbon	57.3	40.6	52.2
Ash	6.9	21.6	10.1
Ultimate analysis, weight-percent:			
Hydrogen	5.1	4.4	5.0
Carbon	78.1	61.9	74.2
Nitrogen	1.6	1.0	1.5
Oxygen	7.1	5.9	7.1
Sulfur	1.2	5.2	2.1
Ash	6.9	21.6	10.1
Calorific value, Btu	13,970	11,190	13,310
Free swelling index	8	2.5	1.5

Table 7
Summary of powerplant data

Type of firing	Rate, 10^3 lb/hr	Pressure, psig	Temperature, °F	Coal fired	Fly ash sample collection conditions	Mercury content of the fly ash, μg Hg/g
Slag top	702	1,268	899	Illinois No. 6 hvcb.	Mechanical collector hopper	0.10 ± 0.02
Slag top	723	1,293	799	Illinois No. 6, hvcb.	Electrostatic precipitator hopper	$.26\pm.04$
Dry bottom	461	1,450	928	Kentucky No. 6, hvbb.	Mechanical dusty collector hopper	$.22\pm.02$

Based on mercury analyses for Illinois No. 6 coal published by the Illinois Geological Survey, the average percentage of the mercury in the original coal accounted for in the ash is 13 percent.

The results seem to indicate that as only 10 to 15 percent of the mercury is retained by the fly ash, 85 to 90 percent of the mercury in the coal could be emitted via the powerplant smoke stacks.

B. Lead and cadmium. The results obtained for cadmium and lead are limited and of a preliminary nature. The longer time required for each analysis and the problems of contamination resulted in less replication. As the result of insufficient replication, most of the results reported do not have statistical errors attached (however, each is the average of at least two values).

Table 8 gives the lead and cadmium assays for Pittsburgh seam coal; table 9 gives the concentration of lead and cadmium found in the ashes from combustion experiments. Table 9 also shows the percentage of the lead and cadmium in the coal that was retained by the ash. The conditions under which the coal was burnt varied with each run, par- ticularly with the 500-lb/hr combustor so that the results of individual runs cannot be compared. It should be noted that cadmium and lead are retained to a greater degree in the ash from the 500-lb/hr combustor than was mercury. This of course could be predicted from relative volatilities.

Table 8
Lead and cadmium content of a
Pittsburgh seam coal ($\pm$1 S.E.)

Lead content, ppm	Number of samples	Cadmium content, ppm	Number of samples
7.7 $\pm$0.5	9	0.14 $\pm$0.05	9

Table 9
Lead and cadmium in fly ash

Combustor	Cadmium in ash, ppm	Cadmium accounted for, percent	Lead in ash, ppm	Lead accounted for, percent
100 g/hr	1.0	68	--	--
100 g/hr	.74	54	71	92
100 g/hr	.99	76	68	93
500 lb/hr	1.22	101	49	72
500 lb/hr	.78	65	44	64
500 lb/hr	.36	37	25	46

C. Copper, chromium, manganese, and nickel. Efforts aimed at defining the behavior of Cu, Cr, Mn, and Ni during specific gravity separation and combustion of coal are in a very preliminary stage. Efforts to date have been aimed at optimizing the analytical procedures and locating and eliminating sources of contamination. One interesting preliminary result presented in table 10 seems to indicate that crushing coal adds significant amounts of manganese to the coal. The jaws of the crushing apparatus were made of a manganese steel. The coal used was a strip coal from the Lennox Bed in Colorado.

Table 10
Analysis of coal before and after crushing, ppm

Element	Concentration before crushing	Concentration after crushing
Cr	3.4	4.3
Cu	3.2	5.4
Mn	4.1	10.3

D. Fluorine. Efforts aimed at analyzing coals for fluorine have been stymied by con-
tamination problems. Sources of fluorine contamination have been located in phosphoric
acid, calcium oxide, boiling chips, and teflon-covered stirring bars. Extreme care
must be taken in the selection of storage containers, and the history of the distilla-
tion apparatus should be known. We believe that we have now located the sources of
error in the fluoride analysis and are in the process of analyzing series of float-sink
samples for their fluoride content.

SUMMARY AND CONCLUSIONS

Our efforts with trace elements in coal have to date met with varying degrees of
success, but certain important conclusions can be drawn from our findings.

First, it would appear that as much as 40 percent of the mercury in the coal is asso-
ciated with the high specific gravity fraction of the coal. Thus if the pyrite is
removed from coal to lower sulfur emissions, a substantial part of the mercury in the
coal is also removed at no extra cost. Second, about 10 to 15 percent of the mercury
from the coal may remain with the fly ash in coal-burning powerplants. Taking both
factors into account could reduce the maximum emission of mercury to about 50 percent
of that present in the coal.

Cadmium and lead are less volatile elements than mercury. As one would expect, the
experimental evidence indicates that they are retained in the fly ash to a greater
extent than is the mercury. As the program continues, other elements that are even
less volatile than lead and cadmium will be investigated, and one would expect them to
be retained in the fly ash to an even greater extent than are lead and cadmium.

Our experience with fluorine, copper, manganese, chromium, and nickel emphasizes the
difficulties inherent in doing trace analyses in matrices as complex as coal. While
care must be exercised in performing any chemical analysis, trace analysis requires
extreme vigilance. In addition to the care required in trace analyses, our studies
have shown that the coal handling procedures themselves may add trace elements to the
coal.